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JAPANESE PATENT OFFICE

## PATENT ABSTRACTS OF JAPAN

(11) Publication number: 07282835 A

(43) Date of publication of application: 27.10.95

(51) Int. Cl

H01M 8/24

H01M 8/12

(21) Application number: 06075154

(22) Date of filing: 13.04.94

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(54) SEALING MATERIAL FOR SOLID ELECTROLYTE  
FUEL CELL, SEALING METHOD FOR SOLID  
ELECTROLYTE FUEL CELL USING THIS  
MATERIAL, AND SOLID ELECTROLYTE FUEL  
CELL

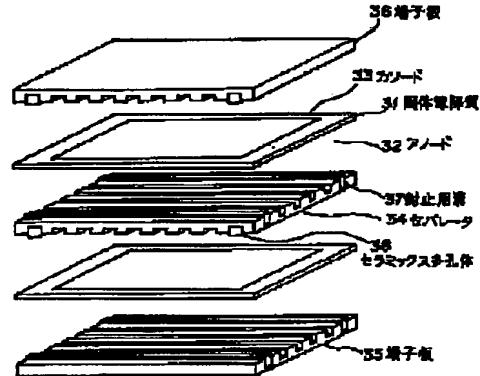
output under high fuel utilization factor is increased.

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### (57) Abstract:

PURPOSE: To elastically absorb or moderate stress or stress-strain caused by difference in thermal expansion between constitution materials to increase cell output under high fuel utilization factor by using a porous insulating ceramics having a specified porosity.

CONSTITUTION: Sealing grooves 37 are formed at specified edges of a separator 34 and terminal plates 35, 36, and sealing members made of a specified sealing material are fit to the grooves. The sealing material made of porous insulating ceramics having a porosity of 70-99% is used. Stability at high temperature is increased, conductivity is decreased to increase insulation, and stress or stress-strain caused by difference in thermal expansion between constituting materials is elastically absorbed or moderated. The sealing is sufficiently made durable to heat cycles, and also durable to load, pressure variation, high differential pressure, prevents gas leak, and cell



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**CLAIMS**

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**[Claim(s)]**

[Claim 1] The closure ingredient for solid oxide fuel cells which consists of the porosity insulation ceramics of 70 - 99% of porosity.

[Claim 2] The closure approach of a solid oxide fuel cell using a closure ingredient according to claim 1.

[Claim 3] The solid oxide fuel cell which changes using a closure ingredient according to claim 1.

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[Translation done.]

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**DETAILED DESCRIPTION**

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**[Detailed Description of the Invention]**

[0001]

[Industrial Application] This invention relates to the closure approach of a solid oxide fuel cell and solid oxide fuel cell using the new closure ingredient for solid oxide fuel cells, and it.

[0002]

[Description of the Prior Art] A fuel cell makes oxidation reaction with fuel gas like a hydrocarbon, and oxidant gas like air perform electrochemically. It is direct conversion equipment which changes the energy change in that case into electrical energy directly. Especially a solid oxide fuel cell Since an edge strip is corroded by the electrolyte, the electrolyte itself does not decompose or an electrolyte does not evaporate unlike the fuel cell of the phosphoric-acid mold which becomes liquefied, or a melting carbonate mold under an ordinary state or actuation conditions Since cell structure is simplified and Japanese lacquer and operating temperature are near 1000 degree C and an elevated temperature, While being able to use it as it is, without reforming inflammable gas, such as natural gas which uses methane besides hydrogen, ethane, a propane, butane, and these low-grade hydrocarbons as a principal component as a fuel, energy use effectiveness can be raised by leading exhaust heat to a gas turbine or a steam turbine. A solid oxide fuel cell is divided roughly into a monotonous mold, cylindrical, and a monolithic mold (or honeycomb mold) based on structure, and the monotonous mold attracts attention from a viewpoint of high power density, low cost, a miniaturization, or miniaturization especially.

[0003] Although conventionally known as a thing equipped with the cylindrical one apparatus manifold about the plate-like solid oxide fuel cell, the strabism explanatory view of one example is shown in drawing 4 . In drawing 4 , the cathode 42 and anode 43 which consist of a porous electrode material are formed in both sides of the solid electrolyte plate 41, the solid electrolyte plate which attached this electrode is accumulated through the separator 44 which served both as the gas passageway and the electric zygote, and terminal assemblies 45 and 46 are arranged by the solid electrolyte plate which attached the lowermost electrode in the topmost part, respectively. While a separator 44 connects inter-electrode [ of the adjoining cel ] electrically Slot 44a is formed in a top face, slot 44b is formed in an inferior surface of tongue, and these slots form the fuel gas path corresponding to the anode side of the adjoining cel, and the oxidant gas path corresponding to a cathode side, respectively. Moreover, Slots 45a and 46b are formed in one side of each terminal assemblies 45 and 46, respectively, and the fuel gas path and the oxidant gas path are formed, respectively. Moreover, the cell of the multistage tandem type which consists of many necessary cels is formed by considering as the same structure as drawing 4 except fluctuating the number of laminatings of a unit cell.

[0004]

[Problem(s) to be Solved by the Invention] By the way, in the above-mentioned conventional monotonous mold fuel cell, the closure member made from an alumina is attached in four corners of a cell proper, and the contact part of a manifold, and the glass softened in operating temperature is usually put and closed between a closure member, a cell proper, and a manifold. However, as stress did not produce a cell proper, a manifold, and a closure member by the differential thermal expansion in the case of such closure structure, although it was necessary to prepare the gap of only the difference of the amount of thermal expansion between each part material, since it was very

difficult to set up the width of face of this spacing correctly beforehand, the local gas leak by this gap was invited, and the fall of a cell output did not escape. Moreover, in the conventional monotonous mold fuel cell, it has a current collection function so that a separator may also be called interconnector. As opposed to being formed with the metal of the quality of the material which suits it, for example, a heat-resistant alloy The sealing agent which a solid electrolyte is formed with the ceramics which makes a zirconia a subject, and is put among both is glass softened in operating temperature like the above. Among these 3 persons By the repeat of the environmental condition which attains to hot cell operating temperature called near 1000 degree C from starting and its fluctuation, especially a heat cycle, since a remarkable difference arises in thermal-expansion properties, such as coefficient of linear expansion Distortion by stress arises among 3 persons, and there is a fault that bonding strength falls further, or a crack occurs, or produce a crevice in a joint, leakage, fuel gas, and oxidant gas carry out [ gas ] cross leak, the function as an active material is spoiled, and a cell output declines. Moreover, since viscosity falls at the time of an elevated temperature, when the above-mentioned glass has a too high pressure concerning the closure section, it has the problem of becoming closure impossible.

[0005] This invention conquers the fault which such a conventional closure ingredient for solid oxide fuel cells has, and is stable also at an elevated temperature. Conductivity is insulation small, and, moreover, the stress or the stress-strain diagram of a thermal-expansion property based on a difference between the components of a cell can be absorbed or eased elastically. Upwards a heat cycle can fully be borne, fluctuation of a load or a pressure and high differential pressure can fully be borne, a gas leak can be prevented, and it is made for the purpose of offering the closure ingredient for solid oxide fuel cells which may improve a cell output under a high fuel utilization rate.

[0006]

[Means for Solving the Problem] this invention persons came to complete this invention for the porosity insulation ceramics with specific porosity suiting that purpose based on a header and this knowledge, as a result of repeating research variously, in order to develop the closure ingredient for solid oxide fuel cells which has the above mentioned desirable property.

[0007] That is, this invention offers the closure ingredient for solid oxide fuel cells which consists of the porosity insulation ceramics of 70 - 99% of (1) porosity. The closure ingredient for solid oxide fuel cells given [ above-mentioned ] in (1) term which consists of the porosity insulation ceramics of 80 - 97% of (2) porosity as a desirable mode, (3) The above (1) whose aperture is 1-100 micrometers, or the closure ingredient for solid oxide fuel cells given in (2) terms, (4) The above (1) whose aperture is 5-50 micrometers, or the closure ingredient for solid oxide fuel cells given in (2) terms, (5) The closure ingredient for solid oxide fuel cells of the above-mentioned (1) - (4) term (1), i.e., the above, which is 2 ohm to 1 cm to less than [ 1 ] thru/or the publication to either of the 10-(4) terms of electrical conductivity, (6) The closure ingredient for solid oxide fuel cells of the above (1) which is 3 ohm to 1 cm to less than [ 1 ] thru/or the publication to either of the 10-(4) terms of electrical conductivity, (7) The porosity insulation ceramics An alumina, a silica, silicon carbide, Beryllia, a mica, a magnesia, boron nitride, forsterite, a steatite, The above (1) which is at least one sort chosen from a mullite, aluminum nitride, and cordierite thru/or the closure ingredient for solid oxide fuel cells given in either of the (6) terms, (8) Closure ingredient \*\* for solid oxide fuel cells of a publication is mentioned to either the above (1) which is the constituent with which the porosity insulation ceramics consists of combination of an alumina and a silica thru/or (6) terms.

[0008] The porosity insulation ceramics which constitutes the closure ingredient of this invention requires that porosity should be 80 - 97% preferably 70 to 99%. Moreover, this ceramics shows elasticity and shows whenever [ corresponding contraction ] according to a load or extent of pressurization. Although various values are taken under a fixed load or pressurization according to the class of ceramics, such as the quality of the material besides the above-mentioned porosity, and an aperture, whenever [ contraction / of this ceramics ] should just apply or pressurize a load so that whenever [ suitable contraction ] may be taken according to the class of ceramics to extent with which the necessary gas closure is attained at the time of cell actuation, in order to make it function as a closure ingredient. If the porosity of this ceramics is too larger than the above-mentioned range, a passage and since [ which become empty ] it becomes that it is hard to change the configuration of a porous body by the load or pressurization elastically even if it becomes, and the amount of gas

leaks increases and porosity is too smaller than the above-mentioned range, gas will become easy to produce a gap for the hole of a porous body in a closure side, and neither of the cases can do sufficient closure. Moreover, the range of 1-100 micrometers of apertures of this ceramics is 5-50 micrometers more preferably. If an aperture is too large, it becomes easy to carry out a gas leak, and even if too small, it will become that it is hard to change the configuration of a porous body elastically, and, in any case, sufficient closure will stop being able to carry out easily.

[0009] Moreover, as for the porosity insulation ceramics, what has sufficient insulation is desirable, electrical conductivity is desirable as such a thing, and ten to 3 ohm to 1 cm to 1 the following are used more preferably ten to 2 ohm to 1 cm to less than [ 1 ]. Since it will become easy to produce an electric short circuit and the cell engine performance will be degraded between separators if electrical conductivity is too large, it is not desirable.

[0010] The constituent which the constituent which consists of an alumina, a silica, silicon carbide, beryllia, a mica, a magnesia, boron nitride, forsterite, a steatite, a mullite, aluminum nitride, cordierites, or these combination, for example is mentioned as the quality of the material of the porosity insulation ceramics, and consists of combination of an alumina and a silica especially is desirable.

[0011] About the solid oxide fuel cell to which the closure ingredient of this invention is applied, although there may not be especially a limit, for example, a cylindrical thing may be used for it, preferably, it is the thing of a monotonous mold and has quadrisection manifold structure also in a monotonous mold still more advantageous. In this monotonous type of thing, the parts by which the closure is carried out with the closure ingredient of this invention are both these preferably, although either between a cell proper and a manifold and between a solid electrolyte plate, a separator, and a terminal assembly are good.

[0012] Next, this invention offers the closure approach of the solid oxide fuel cell which used the closure ingredient of a publication for either (9) above (1) thru/or (8) terms.

[0013] One desirable as this closure approach carries out two or more laminatings of the solid electrolyte plate with which the electrode was prepared in (10) both sides through a separator. On the side face of the cell proper which comes to arrange a terminal assembly in this solid electrolyte plate of both ends, respectively The solid oxide fuel cell which comes to equip the manifold in which supply and the discharge path of fuel gas and oxidant gas were formed In the approach of closing by making a closure object intervene between this cell proper and a manifold and between a solid electrolyte plate, a separator, and a terminal assembly the closure approach of the solid oxide fuel cell characterized by using the closure object which consists of a closure ingredient of said this invention as a closure object made to intervene between a cell proper and a manifold and/or between a solid electrolyte plate, a separator, and a terminal assembly -- it comes out.

[0014] In this approach, it is suitably carried out by making a gasket placed between those closure parts about the closure between a cell proper and a manifold again by attaching the closure object which fabricated the closure ingredient in the suitable configuration about the closure between a solid electrolyte plate and a separator along the flow direction of predetermined gas to the both-ends edge of both sides of a separator which touch predetermined gas, and one side of each terminal assembly. The attachment of this closure object between a cell proper, between manifolds or a solid electrolyte plate, a separator, and a terminal assembly about that either Although it may carry out by making a glass closure object intervene, this closure object may be softened at the time of actuation and adhesion junction may be carried out, it is desirable that it is because the closure object which establishes the slot for the closures in a separator and the predetermined edge section of each terminal assembly, and becomes this from the closure ingredient of this invention is inserted in and it fixes. therefore, the closure approach of the solid oxide fuel cell characterized by using for the most desirable one as an embodiment in this invention approach the closure object which becomes either the above (1) thru/or (8) terms from the closure ingredient of a publication as a closure object made to intervene between (11) cells proper and a manifold and between a solid electrolyte plate, a separator, and a terminal assembly -- it comes out.

[0015] Next, this invention offers the solid oxide fuel cell which grows into either (12) above (1) thru/or (8) terms using the closure ingredient of a publication.

[0016] One desirable as this fuel cell carries out two or more laminatings of the solid electrolyte

plate with which the electrode was prepared in (13) both sides through a separator. On the side face of the cell proper which comes to arrange a terminal assembly in this solid electrolyte plate of both ends, respectively In the solid oxide fuel cell which equip with the manifold in which supply and the discharge path of fuel gas and oxidant gas were formed, and a closure object is made to intervene between this cell proper and a manifold and between a solid electrolyte plate, a separator, and a terminal assembly, and changes the solid oxide fuel cell characterized by being the closure object with which the closure object made to intervene between a cell proper and a manifold and/or between a solid electrolyte plate, a separator, and a terminal assembly becomes either the above (1) thru/or (8) terms from the closure ingredient of a publication -- it comes out.

[0017] In the solid oxide fuel cell of such a monotonous mold preferably (14) as the monotonous mold solid oxide fuel cell given [ aforementioned ] in (13) terms characterized by closing between [ both ] between a cell proper and a manifold and a solid electrolyte plate, a separator, and a terminal assembly, and a still more desirable mode (15) as a monotonous mold solid oxide fuel cell the above (13) which has a quadrisection mold manifold, or given in (14) terms, and most desirable mode (16) Monotonous mold solid oxide fuel cell \*\* given [ aforementioned ] in (15) terms in which pressed down through the spring member to each manifold, and the plate was made to arrange is mentioned. It is desirable to use for a spring function what does not produce degradation with suitable gestalten, such as a coil spring, a flat spring, and a pan spring, also with operating temperature of a cell like silicon nitride as this spring member. It may bind tight with a bolt nut or this presser-foot plate may be pressurized by external force from the outside of a presser-foot plate so that opposite arrangement may be carried out at spacing at which suitable pressurization is energized by the spring member made to intervene, and it may be fixed in that arrangement part and it may be in such an arrangement condition. Pressurization by this external force is performed with oil pressure, pneumatic pressure, etc.

[0018] In this invention, a suitable solid oxide fuel cell is explained below. First, about each part material, a solid electrolyte plate will not be restricted especially if it has oxygen ion conductivity, for example, well-known solid electrolytes, such as fully stabilized zirconia like yttria stabilized zirconia (YSZ) and calcia fully stabilized zirconia (CSZ) and partially stabilized zirconia, are mentioned.

[0019] Since it is an oxidant gas paths side, such as oxygen and air, a cathode applies to solid electrolyte plate one side conductive multiple oxide powder, such as the conductive ingredient 3 which has corrosion resistance to oxidant gas under an elevated temperature, for example,  $\text{LaxSr}_{1-x}\text{MnO}$  etc., and it is formed in the shape of porosity so that it may become gas permeability. A brushing method, screen printing, etc. are used as this method of application. In addition, as the creation approach to the solid electrolyte plate of the cathode of the porosity-like film, a CVD method, a plasma-CVD method, a spatter, a spraying process, etc. are usable.

[0020] Using the conductive ingredient which has corrosion resistance to fuel gas under an elevated temperature, for example, nickel/ZrO<sub>2</sub> cermet etc., since an anode is a fuel gas paths side, such as hydrogen, it is created by solid electrolyte plate one side with the application of the same porosity-like film forming method as a cathode.

[0021] Thus, two or more solid electrolyte plates in which each electrode, i.e., an anode, and a cathode were formed to both sides are prepared, these are accumulated through a separator, and the cell of the multistage tandem type which consists of many cel is created by arranging a terminal assembly in this solid electrolyte plate of both ends, respectively. Like drawing 4 , while a separator 44 connects inter-electrode [ of the adjoining cel ] electrically, each gas passageway by the side of the anode of the cel which a slot is established in both sides and adjoins, and a cathode, i.e., fuel gas path 44a, and oxidant gas path 44b are formed. Although each slot will not be restricted especially if fuel gas and oxidant gas can be supplied, but a configuration, arrangement, etc. can be selected suitably, as usually shown in drawing 4 , each gas passageways 44a and 44b prepared in the top face of a separator and an inferior surface of tongue are mutually arranged in the direction of a right angle. Thus, if it arranges, the inlet port of fuel gas and an outlet, the inlet port of oxidant gas, and an outlet can be arranged on the respectively same field after accumulating a cel, and the configuration of gas supply and an excretory system can be made easy and easy as an accumulation cel.

[0022] When accumulating and assembling the solid electrolyte plate 41 which prepared the

electrode, a separator 44, and each terminal assemblies 45 and 46 like drawing 4 , it is necessary to close so that there may be no leakage of gas (leak) between the solid electrolyte plate 41, a separator 44, or each terminal assemblies 45 and 46.

[0023] The gestalt which inserted in this slot the closure object which the closure ingredient of this invention was used suitably because of the closure between such a solid electrolyte plate, a separator, and a terminal assembly, established the slot for the closures in the both-ends edge on that field along with each gas passageway in the separator and the terminal assembly, and size was made to match this as that suitable use gestalt, and fabricated the closure ingredient, and was fixed is mentioned. Moreover, when the closure ingredient of this invention is used for the closure between a cell proper and a manifold so that it may mention later, the aforementioned closure is good also by pasting up with the inorganic adhesive of for example, a zirconia system, and closing with the glass plate and glass paste whose softening temperature is about 800 degrees C. It softens moderately in the operating temperature (about 900-1000 degrees C) of a cell, and this glass plate and glass paste close gas.

[0024] In this way, what is necessary is just to attach a manifold in those fields, since it is arranged so that the both ends of each gas passageways 44a and 44b of a cell may come to the same side, respectively in order to supply fuel gas and oxidant gas to the assembled cell. For example, as shown in drawing 4 , the accumulation mold cell proper assembled as mentioned above is inserted into the cylinder of a cylindrical manifold (M). By arranging so that the outlet of Slots 44a and 44b may face a cylinder wall, and closing the contiguity part (four places) of a cell proper and a manifold It will correspond with a discharge fuel gas path, four gas passageways, i.e., the supply fuel gas path, in which each both ends of each gas passageways 44a and 44b were formed with the cylinder wall and cell proper of a manifold, respectively, a supply oxidant gas path, and a discharge oxidant gas path. The closure ingredient of this invention is used suitably because of the closure between such a cell proper and a manifold again.

[0025] Especially a desirable thing makes it arrange as a solid oxide fuel cell of this invention, four manifolds, i.e., the quadrisection mold manifold, which counters four side faces of said cell proper. As a quadrisection mold manifold, a core box manifold is desirable. A gasket is made to usually intervene between a cell proper and a core box manifold.

[0026] The transverse-plane cross-section schematic diagram of one example of the solid oxide fuel cell which arranged this core box manifold and gasket is shown in drawing 2 . While being prepared on the base plate 29 through the glass sheet 24 which the core box manifold 22 softens with a cell proper 21 in the center section, and softens in both the operating temperature of a cell on the both sides, a gasket 23 is made to intervene between a cell proper 21 and the core box manifold 22, it presses down at still more suitable spacing for the periphery of the inner of the core box manifold 22, and a fixture 26 is fixed, and is prepared, it presses down with the core box manifold 22, and the silicon nitride spring 25 is made to intervene between fixtures 26 in drawing 2 . In this way, gasket \*\*\*\*\* will be energized by the cell proper according to the suppression force of a spring, and a core box manifold will be forced. The base plate 29 is penetrated in each manifold, and the fuel gas charging line 27 and the fuel gas discharge piping 28 are connected to it. Like each part material, such as a manifold arranged in the above right and left, also forward and backward, each part material, such as a manifold, is arranged, the base plate 29 is penetrated also to each of this manifold, and an oxidant gas charging line and oxidant gas discharge piping are connected to it.

[0027]

[Effect of the Invention] The remarkable effectiveness that the stress based on [ the closure ingredient for the solid oxide fuel cells of this invention is stable also at an elevated temperature, and conductivity is small, are insulation, and ] the difference in the thermal-expansion property between the components of a cell moreover or a stress-strain diagram can be absorbed or eased elastically, a heat cycle can fully be borne upwards, fluctuation of a load or a pressure and high differential pressure can fully be borne, a gas leak can be prevented, and a cell output may be improved under a high fuel utilization rate is done so.

[0028]

[Example] Hereafter, an example explains this invention to a detail.

According to the set format of the accumulation cel of example 1 drawing 1 , the solid oxide fuel cell

of a ten-step serial cel was manufactured. the solid electrolyte plate 11 -- yttria -- three-mol % -- the 100x100x0.2mm tabular object which consists of partially stabilized zirconia which is an added zirconia was used. And La0.9Sr0.1MnO<sub>3</sub> powder (mean particle diameter of about 5 micrometers) was applied to 0.1mm in thickness by the brushing method at the oxygen path side, and it considered as the cathode 13, and the cermet mixing powder of nickel/ZrO<sub>2</sub> (10/1-fold quantitative ratio) was applied to 0.1mm in thickness by the brushing method, and it considered as the anode 12 at the hydrogen path side. Inconel 600 was used for a separator 14 and terminal assemblies 15 and 16. The dimension of a separator and a terminal assembly was made into height of 2.4mm, and 0.5mm of depth of flute by 100x100mm.

[0029] The laminating of this solid electrolyte plate 11 and separator 14 was carried out by turns, the terminal assembly was arranged in this solid electrolyte plate of both ends, respectively, and softening temperature carried out to the gas closures on both sides of the glass plate which is about 800 degrees C between the solid electrolyte plate 11, a separator 14, and terminal assemblies 15 and 16. What has reducibility-proof in this glass plate to hydrogen with the operating temperature (1000 degrees C) of a cell, and has oxidation resistance to air, and has waterproof steam nature is chosen. It softens in the operating temperature of a cell and this glass plate closes gas.

[0030] In this way, the manifold was installed in the accumulated cell like drawing 2 , and it had the presentation of 240 % of the weight of SiO(s) with a thickness of 1mm, and 2O360 % of the weight of aluminum between the manifold and the cell, and porosity forced the manifold on the cell proper by pressurization 1.0 kgf/cm<sup>2</sup> to a gasket side oppressively, while electrical conductivity put the ceramic porous body of 10-5ohm-1cm-1 at 90% and considered as the gasket. This forcing was performed on a manifold and its outside by [ which carried out fixed installation ] pressing down and making an energization spring like a silicon nitride spring intervene between fixtures. Platinum lead wire was welded to the electric takeoff connection, and it connected with it electrically.

[0031] Thus, the produced solid oxide fuel cell was heated. A room temperature to 150 degrees C carried out the temperature up by 1 degree C / min, and the solvent of a spreading electrode was evaporated. 150-350 degrees C carried out the temperature up by 1.5 degrees C / min. Above 350 degrees C, in order to prevent oxidation of an anode, the temperature up of the nitrogen gas was carried out to the hydrogen path side to 1000 degrees C by the sink, and 1 degree C / min.

[0032] After amounting to 1000 degrees C, when the gas outlet flow rate was measured with the film flowmeter, the anode and cathode side of the amount of external leaks was about 1 - 2%. Then, it held at 1000 degrees C, and hydrogen was started to the anode side and the sink and the generation of electrical energy were started for oxygen to the cathode side. Open circuit voltage was 12.5V and gas cross leak was 0.1% or less from hydrogen. The discharge property of this cell is shown in Table 1.

[0033]

[Table 1]

電圧 (V)	電流 (A)
12.5	0.0
11.0	0.8
10.0	2.1
9.0	6.3
8.0	11.3
7.0	16.0

[0034] Next, it became 82% when the maximum fuel utilization rate of this cell was measured.

[0035] According to the set format of example 2 drawing 3 , the solid oxide fuel cell of a ten-step serial cel was manufactured. the solid electrolyte plate 31 -- yttria -- three-mol % -- the 100x100x0.2mm tabular object which consists of partially stabilized zirconia which is an added zirconia was used. And La0.9Sr0.1MnO<sub>3</sub> powder (mean particle diameter of about 5 micrometers) was applied to 0.1mm in thickness by the brushing method at the oxygen path side, and it considered as the cathode 33, and the cermet mixing powder of nickel/ZrO<sub>2</sub> (10/1-fold quantitative ratio) was applied to 0.1mm in thickness by the brushing method, and it considered as the anode 32 at the hydrogen path side. Inconel 600 was used for a separator 34 and terminal assemblies 35 and 36. The dimension of a separator and a terminal assembly was made into height of 2.4mm, and 0.5mm of

depth of flute by 100x100mm. Moreover, along with the predetermined gas passageway, the slot 37 for the closures was established in the both ends of both sides of a separator 34, and one side of terminal assemblies 35 and 36, and the depth was set to 0.8mm.

[0036] Accumulate this solid electrolyte plate 31 and separator 34 by turns, and terminal assemblies 35 and 36 are arranged in this solid electrolyte plate of both ends, respectively. Between the solid electrolyte plate 31, a separator 34, and terminal assemblies 35 and 36 It has the presentation of 240 % of the weight of SiO(s) with a thickness of 1mm, and 2O360 % of the weight of aluminum, and porosity inserted the ceramic porous body 38 of 10-5ohm-1cm-1 in the slot 37 for the closures at 90%, and electrical conductivity considered as the gasket.

[0037] In this way, the manifold was installed in the accumulated cell like drawing 2 , and softening temperature carried out to the gas closures on both sides of the glass plate which is about 800 degrees C between the manifold and the cell. What has reducibility-proof in this glass plate to hydrogen with the operating temperature (1000 degrees C) of a cell, and has oxidation resistance to air, and has waterproof steam nature is chosen. It softens in the operating temperature of a cell and this glass plate closes gas. Platinum lead wire was welded to the electric takeoff connection, and it connected with it electrically.

[0038] Thus, the produced solid oxide fuel cell was heated. A room temperature to 150 degrees C carried out the temperature up by 1 degree C / min, and the solvent of a spreading electrode was evaporated. 150-350 degrees C carried out the temperature up by 1.5 degrees C / min. Above 350 degrees C, in order to prevent oxidation of an anode, the temperature up of the nitrogen gas was carried out to the hydrogen path side to 1000 degrees C by the sink, and 1 degree C / min.

[0039] After amounting to 1000 degrees C, when the gas outlet flow rate was measured with the film flowmeter, the anode and cathode side of the amount of external leaks was about 5 - 7%. Then, it held at 1000 degrees C, and hydrogen was started to the anode side and the sink and the generation of electrical energy were started for oxygen to the cathode side. Open circuit voltage was 12V and the amount of gas cross leaks was 0.02% or less from hydrogen. The discharge property of this cell is shown in Table 2.

[0040]

[Table 2]

電圧 (V)	電流 (A)
12.0	0.0
11.0	0.5
10.0	1.2
9.0	3.0
8.0	9.1
7.0	13.3

[0041] Next, it became 70% when the maximum fuel utilization rate of this cell was measured.

[0042] According to the set format of example 3 drawing 3 , the solid oxide fuel cell of a ten-step serial cel was manufactured. the solid electrolyte plate 31 -- yttria -- three-mol % -- the 100x100x0.2mm tabular object which consists of partially stabilized zirconia which is an added zirconia was used. And La0.9Sr0.1MnO<sub>3</sub> powder (mean particle diameter of about 5 micrometers) was applied to 0.1mm in thickness by the brushing method at the oxygen path side, and it considered as the cathode 33, and the cermet mixing powder of nickel/ZrO<sub>2</sub> (10/1-fold quantitative ratio) was applied to 0.1mm in thickness by the brushing method, and it considered as the anode 32 at the hydrogen path side. Inconel 600 was used for a separator 34 and terminal assemblies 35 and 36. The dimension of a separator and a terminal assembly was made into height of 2.4mm, and 0.5mm of depth of flute by 100x100mm. Moreover, along with the predetermined gas passageway, the slot 37 for the closures was established in the both ends of both sides of a separator 34, and one side of terminal assemblies 35 and 36, and the depth was set to 0.8mm.

[0043] Accumulate this solid electrolyte plate 31 and separator 34 by turns, and terminal assemblies 35 and 36 are arranged in this solid electrolyte plate of both ends, respectively. Between the solid electrolyte plate 31, a separator 34, and terminal assemblies 35 and 36 It has the presentation of 240 % of the weight of SiO(s) with a thickness of 1mm, and 2O360 % of the weight of aluminum, and porosity inserted the ceramic porous body 38 of 10-5ohm-1cm-1 in the slot 37 for the closures at

90%, and electrical conductivity considered as the gasket.

[0044] In this way, the manifold was installed in the accumulated cell like drawing 2, and it had the presentation of 240 % of the weight of SiO(s) with a thickness of 1mm, and 20360 % of the weight of aluminum between the manifold and the cell, and porosity forced the manifold on the cell proper by pressurization 1.0 kgf/cm<sup>2</sup> to a gasket side oppressively, while electrical conductivity put the ceramic porous body of 10-5ohm-1cm<sup>-1</sup> at 90% and considered as the gasket. This forcing was performed on a manifold and its outside by [ which carried out fixed installation ] pressing down and making an energization spring like a silicon nitride spring intervene between fixtures. Platinum lead wire was welded to the electric takeoff connection, and it connected with it electrically.

[0045] Thus, the produced solid oxide fuel cell was heated. A room temperature to 150 degrees C carried out the temperature up by 1 degree C / min, and the solvent of a spreading electrode was evaporated. 150-350 degrees C carried out the temperature up by 1.5 degrees C / min. Above 350 degrees C, in order to prevent oxidation of an anode, the temperature up of the nitrogen gas was carried out to the hydrogen path side to 1000 degrees C by the sink, and 1 degree C / min.

[0046] After amounting to 1000 degrees C, when the gas outlet flow rate was measured with the film flowmeter, the anode and cathode side of the amount of external leaks was about 1 - 2%. Then, it held at 1000 degrees C, and hydrogen was started to the anode side and the sink and the generation of electrical energy were started for oxygen to the cathode side. Open circuit voltage was 12.7V and the amount of gas cross leaks was 0.02% or less from hydrogen. The discharge property of this cell is shown in Table 3.

[0047]

[Table 3]

電圧 (V)	電流 (A)
12.7	0.0
11.0	1.2
10.0	3.0
9.0	7.2
8.0	14.4
7.0	22.0

[0048] Next, it became 87% when the maximum fuel utilization rate of this cell was measured.

[0049] Installing the cell by the conventional approach as shown in example drawing 4 of a comparison, the amount of external leaks was [ 11.5V and the amount of gas cross leaks of open circuit voltage ] about 3% from hydrogen about 1% in the measurement same in the ten-step serial cel using glass (less than 0.1% of porosity) as a sealing agent as an example 1. The discharge property of this cel is shown in Table 4.

[0050]

[Table 4]

電圧 (V)	電流 (A)
11.5	0.0
10.0	0.8
9.0	1.5
8.0	7.2
7.0	10.8

[0051] Next, when the maximum fuel utilization rate of this cel was measured, it was as low as 60%.

---

[Translation done.]

**\* NOTICES \***

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**DESCRIPTION OF DRAWINGS**

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**[Brief Description of the Drawings]**

**[Drawing 1]** The decomposition explanatory view showing the set format of one example of a monotonous mold solid oxide fuel cell.

**[Drawing 2]** The transverse-plane cross-section schematic diagram of one example of the suitable monotonous mold solid oxide fuel cell of this invention.

**[Drawing 3]** The decomposition explanatory view showing the set format of one example of the monotonous mold solid oxide fuel cell of this invention.

**[Drawing 4]** The strabism explanatory view of one example of the monotonous mold solid oxide fuel cell equipped with the cylindrical mold manifold.

**[Description of Notations]**

11, 31, 41 Solid electrolyte plate

12, 32, 42 Anode

13, 33, 43 Cathode

14, 34, 44 Separator

14a, 44a Fuel gas path

14b, 44b Oxidant gas path

15, 16, 35, 36, 45, 46 Terminal assembly

21 Cell Proper

22 Core Box Manifold

23 Gasket

24 Glass Sheet

25 Silicon Nitride Spring

26 Presser-Foot Fixture

27 Fuel Gas Charging Line

28 Fuel Gas Discharge Piping

29 Base Plate

37 Slot for Closures

38 Ceramic Porous Body

M Cylindrical manifold

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[Translation done.]

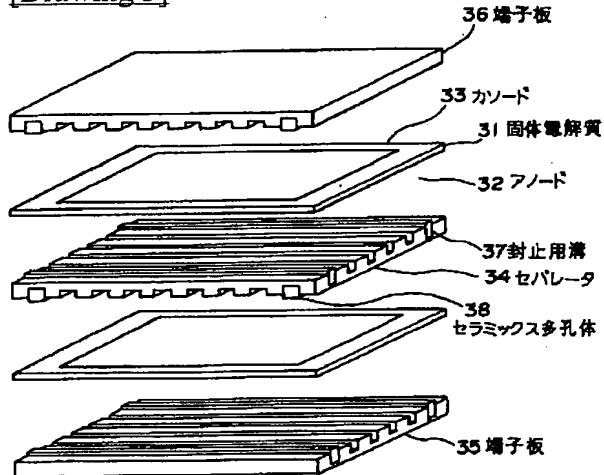
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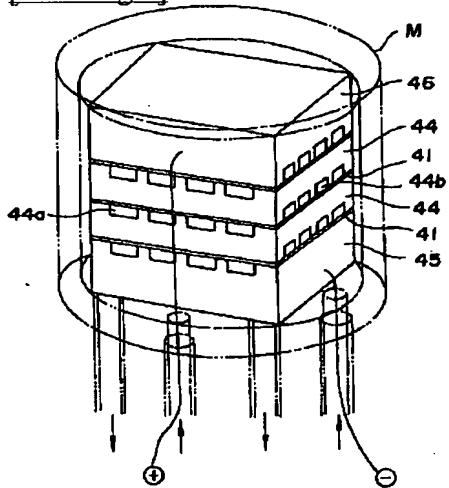
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## DRAWINGS

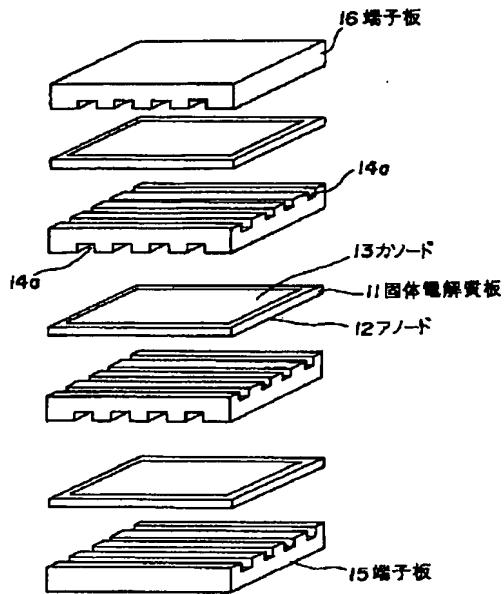
[Drawing 3]



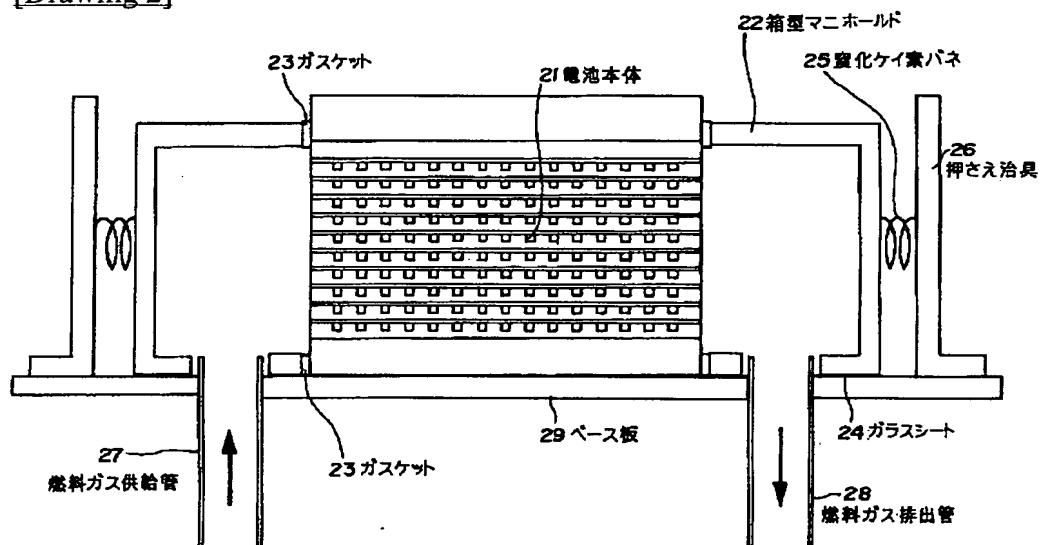
[Drawing 4]



[Drawing 1]



[Drawing 2]



[Translation done.]

(19) 日本国特許庁 (JP)

(12) **公開特許公報 (A)**

(11) 特許出願公開番号

特開平7-282835

(43) 公開日 平成7年(1995)10月27日

(51) Int. C.I.<sup>6</sup> 識別記号 庁内整理番号 F I 技術表示箇所  
H 01 M 8/24 M 9444-4 K  
8/12 9444-4 K

審査請求 未請求 請求項の数 3 O L (全 8 頁)

(21) 出願番号 特願平6-75154

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最終頁に続く

(54) 【発明の名称】 固体電解質型燃料電池用封止材料、それを用いた固体電解質型燃料電池

(57) 【要約】

【構成】 多孔度70~99%の多孔質絶縁性セラミックスから成る固体電解質型燃料電池用封止材料、それを用いた固体電解質型燃料電池の封止方法及び固体電解質型燃料電池である。

【効果】 封止材料は、高温でも安定で、導電率が小さく絶縁性であり、しかも電池の構成材料間の熱膨張特性の差異に基づく応力あるいは応力歪みを弾性的に吸収あるいは緩和でき、熱サイクルに十分に耐えうる上に、荷重あるいは圧力の変動、高い差圧に十分に耐えることができ、ガスリークを防止でき、高い燃料利用率下で電池出力を向上しうる。

## 【特許請求の範囲】

【請求項1】 多孔度70～99%の多孔質絶縁性セラミックスから成る固体電解質型燃料電池用封止材料。

【請求項2】 請求項1記載の封止材料を用いた固体電解質型燃料電池の封止方法。

【請求項3】 請求項1記載の封止材料を用いて成る固体電解質型燃料電池。

## 【発明の詳細な説明】

## 【0001】

【産業上の利用分野】 本発明は、新規な固体電解質型燃料電池用封止材料、それを用いた固体電解質型燃料電池の封止方法及び固体電解質型燃料電池に関するものである。

## 【0002】

【従来の技術】 燃料電池は、炭化水素のような燃料ガスと空気のような酸化剤ガスとの酸化反応を電気化学的に行わせ、その際のエネルギー変化を直接に電気エネルギーに変換する直接発電装置であり、中でも固体電解質型燃料電池は、電解質が常態あるいは作動条件下で液状となるリン酸型や溶融炭酸塩型の燃料電池と異なり、電解質により周辺部材が腐食されたり、電解質自身が分解したり、蒸発することができないので、電池構造を簡素化しうるし、また、作動温度が1000°C付近と高温であるため、燃料として水素の他、メタン、エタン、プロパン、ブタン、これら低級炭化水素を主成分とする天然ガスなどの可燃性ガスを改質することなくそのまま使用しうるとともに、排熱をガスバービンや蒸気タービンに導くことにより、エネルギー利用効率を高めうる。固体電解質型燃料電池は、構造に基づき、平板型、円筒型、モノリシック型（又はハニカム型）に大別され、中でも平板型が高出力密度、低コスト、小型化あるいはコンパクト化の観点から注目されている。

【0003】 平板状固体電解質型燃料電池について、円筒状一体型マニホールドを備えたものとして従来知られているものの1例の斜視説明図を図4に示す。図4において、固体電解質板41の両面には、多孔性電極材料からなるカソード42及びアノード43が形成され、この電極を付設した固体電解質板は、ガス通路と電気的接合部を兼ねたセバレータ44を介して集積され、最上部及び最下部の、電極を付設した固体電解質板には、端子板45及び46がそれぞれ配設されている。セバレータ44は隣接するセルの電極間を電気的に接続するとともに、上面に溝44a、下面に溝44bが形成され、これらの溝はそれぞれ隣接するセルのアノード側に対応する燃料ガス通路及びカソード側に対応する酸化剤ガス通路を形成し、また、各端子板45及び46の片面にはそれぞれ溝45a及び46bが形成され、それぞれ燃料ガス通路及び酸化剤ガス通路を形成している。また、単位セルの積層数を増減する以外、図4と同様の構造とすることにより、所要の多数のセルからなる多段直列型の電池

が形成される。

## 【0004】

【発明が解決しようとする課題】 ところで、上記従来の平板型燃料電池においては、通常、電池本体の4隅とマニホールドの接触箇所に、アルミナ製の封止部材を取り付け、封止部材と電池本体及びマニホールド間に、作動温度で軟化するガラスを挟み込んで封止している。しかしながら、このような封止構造の場合、電池本体とマニホールド及び封止部材は、熱膨張差により応力が生じないように、各部材間に熱膨張量の差だけの間隙を設けることが必要になるが、この間隔の幅をあらかじめ正確に設定するのは極めて困難なので、この間隙による局所的なガスリークを招来し、電池出力の低下が免れなかった。また、従来の平板型燃料電池では、セバレータがインターフェクタとも称されるように集電機能を有し、それに適合するような材質の金属、例えば耐熱合金で形成されているのに対し、固体電解質はジルコニアを主体とするセラミックスで形成され、また両者間に挟み込まれる封止材は上記と同様に作動温度で軟化するガラスであり、これら3者間には、立ち上げから1000°C付近という高温の電池作動温度に及ぶ環境条件及びその変動、特に熱サイクルの繰り返しにより、線膨張係数などの熱膨張特性にかなりの差異が生じるので、3者間には応力による歪が生じ、さらには接合強度が低下したり、クラックが発生したり、接合部にすき間を生じてガスが漏れ、燃料ガスと酸化剤ガスがクロスリークして活物質としての機能がそこなわれ電池出力が低下するという欠点がある。また、上記ガラスは高温時には粘度が低下するため、封止部にかかる圧力が高すぎると封止不能になるという問題がある。

【0005】 本発明は、このような従来の固体電解質型燃料電池用封止材料のもつ欠点を克服し、高温でも安定で、導電率が小さく絶縁性であり、しかも電池の構成材料間の熱膨張特性の差異に基づく応力あるいは応力歪みを弾性的に吸収あるいは緩和でき、熱サイクルに十分に耐えうる上に、荷重あるいは圧力の変動、高い差圧に十分に耐えることができ、ガスリークを防止でき、高い燃料利用率下で電池出力を向上しうる固体電解質型燃料電池用封止材料を提供することを目的としてなされたものである。

## 【0006】

【課題を解決するための手段】 本発明者らは、前記した好ましい特性を有する固体電解質型燃料電池用封止材料を開発するために種々研究を重ねた結果、特定の多孔度をもつ多孔質絶縁性セラミックスがその目的に適合しうることを見出し、この知見に基づいて本発明を完成するに至った。

【0007】 すなわち、本発明は、(1) 多孔度70～99%の多孔質絶縁性セラミックスから成る固体電解質型燃料電池用封止材料を提供するものである。好ましい

態様として、(2) 多孔度8.0～9.7%の多孔質絶縁性セラミックスから成る上記(1)項記載の固体電解質型燃料電池用封止材料、(3) 孔径が1～100μmである上記(1)又は(2)項記載の固体電解質型燃料電池用封止材料、(4) 孔径が5～50μmである上記

(1)又は(2)項記載の固体電解質型燃料電池用封止材料、(5) 電気伝導度が $10^{-2}\Omega^{-1}\text{cm}^{-1}$ 以下である上記(1)～(4)項すなわち上記(1)ないし(4)項のいずれかに記載の固体電解質型燃料電池用封止材料、(6) 電気伝導度が $10^{-3}\Omega^{-1}\text{cm}^{-1}$ 以下である上記(1)ないし(4)項のいずれかに記載の固体電解質型燃料電池用封止材料、(7) 多孔質絶縁性セラミックスが、アルミナ、シリカ、炭化ケイ素、ベリリア、マイカ、マグネシア、窒化ホウ素、フォルステライト、ステアタイト、ムライト、窒化アルミニウム、コージェライト、あるいはこれらの組合せからなる組成物などが挙げられ、特にアルミナとシリカの組合せからなる組成物が好ましい。

【0008】本発明の封止材料を構成する多孔質絶縁性セラミックスは、多孔度が7.0～9.9%、好ましくは8.0～9.7%であることが必要である。また、このセラミックスは、弹性を示し、荷重や加圧の程度に応じ、相当する収縮度を示すものである。このセラミックスの収縮度は、一定の荷重や加圧下において、上記多孔度の他、材質、孔径などのセラミックスの種類により様々な値をとるが、封止材料として機能させるには、電池作動時ににおいて所要のガス封止が達成される程度にセラミックスの種類に応じ適切な収縮度をとるように荷重をかけあるいは加圧すればよい。このセラミックスの多孔度が上記範囲より大きすぎるとガスが多孔体の孔を通りやすくなつてガスリーク量が多くなるし、また多孔度が上記範囲より小さすぎても荷重や加圧によって多孔体の形状を弾性的に変化させにくくなるため、封止面に間隙を生じやすくなり、いずれの場合も十分な封止ができない。また、このセラミックスの孔径は、好ましくは1～100μm、より好ましくは5～50μmの範囲である。孔径が大きすぎるとガスリークしやすくなるし、また小さすぎても多孔体の形状を弾性的に変化させにくくなり、いずれの場合も十分な封止がしにくくなる。

【0009】また、多孔質絶縁性セラミックスは、十分な絶縁性を有するものが好ましく、このようなものとしては、電気伝導度が好ましくは $10^{-2}\Omega^{-1}\text{cm}^{-1}$ 以下、より好ましくは $10^{-3}\Omega^{-1}\text{cm}^{-1}$ 以下のものが用いられる。電気伝導度が大きすぎるとセパレータ間ににおいて電気短絡を生じやすくなり、電池性能を劣化させるので好ましくない。

【0010】多孔質絶縁性セラミックスの材質として

は、例えばアルミナ、シリカ、炭化ケイ素、ベリリア、マイカ、マグネシア、窒化ホウ素、フォルステライト、ステアタイト、ムライト、窒化アルミニウム、コージェライト、あるいはこれらの組合せからなる組成物などが挙げられ、特にアルミナとシリカの組合せからなる組成物が好ましい。

【0011】本発明の封止材料が適用される固体電解質型燃料電池については、特に制限はなく、例えば円筒型のものでもよいが、好ましくは、平板型のものであり、さらに有利には平板型の中でも四分割マニホールド構造をもつものである。この平板型のものにおいて、本発明の封止材料により封止される箇所は、電池本体とマニホールド間及び固体電解質板とセパレータ及び端子板間のいずれかでもよいが、好ましくはこれら両方である。

【0012】次に、本発明は、(9)前記(1)ないし(8)項のいずれかに記載の封止材料を用いた固体電解質型燃料電池の封止方法を提供するものである。

【0013】この封止方法として好ましいのは、(1) 0) 両面に電極が設けられた固体電解質板をセパレータを介して複数積層し、両端の該固体電解質板にそれぞれ端子板を配設してなる電池本体の側面に、燃料ガス及び酸化剤ガスの供給及び排出通路を形成したマニホールドを装着してなる固体電解質型燃料電池を、該電池本体とマニホールド間、及び固体電解質板とセパレータ及び端子板間に封止体を介在させることにより封止する方法において、電池本体とマニホールド間及び/又は固体電解質板とセパレータ及び端子板間に介在させる封止体として、前記本発明の封止材料からなる封止体を用いることを特徴とする固体電解質型燃料電池の封止方法、である。

【0014】この方法において、固体電解質板とセパレータ間の封止については、封止材料を適切な形状に成形した封止体を、所定ガスの流れ方向に沿い、所定ガスと接する、セパレータの両面及び各端子板の片面の両端縁部に付設することにより、また電池本体とマニホールド間の封止については、その封止箇所にガスケットを介在させることにより、好適に行われる。この封止体の付設は、電池本体とマニホールド間か、あるいは固体電解質板とセパレータ及び端子板間かのいずれかについて、ガ

40 ラス封止体を介在させることにより行い、該封止体を作動時に軟化させ付着接合させてもよいが、セパレータ及び各端子板の所定端縁部に封止用溝を設け、これに本発明の封止材料からなる封止体をはめ込んで固定することによるのが好ましい。よって、本発明方法における実施態様として最も好ましいのは、(11)電池本体とマニホールド間及び固体電解質板とセパレータ及び端子板間に介在させる封止体として前記(1)ないし(8)項のいずれかに記載の封止材料からなる封止体を用いることを特徴とする固体電解質型燃料電池の封止方法、である。

【0015】次に、本発明は、(12)前記(1)ないし(8)項のいずれかに記載の封止材料を用いて成る固体電解質型燃料電池を提供するものである。

【0016】この燃料電池として好ましいのは、(13)両面に電極が設けられた固体電解質板をセパレータを介して複数積層し、両端の該固体電解質板にそれぞれ端子板を配設してなる電池本体の側面に、燃料ガス及び酸化剤ガスの供給及び排出通路を形成したマニホールドを装着し、かつ該電池本体とマニホールド間、及び固体電解質板とセパレータ及び端子板間に封止体を介在させて成る固体電解質型燃料電池において、電池本体とマニホールド間及び/又は固体電解質板とセパレータ及び端子板間に介在させた封止体が、前記(1)ないし(8)項のいずれかに記載の封止材料からなる封止体であることを特徴とする固体電解質型燃料電池、である。

【0017】このような平板型の固体電解質型燃料電池において、好ましくは、(14)電池本体とマニホールド間及び固体電解質板とセパレータ及び端子板間双方を封止することを特徴とする前記(13)項記載の平板型固体電解質型燃料電池、さらに好ましい態様として、

(15)四分割型マニホールドを有する前記(13)又は(14)項記載の平板型固体電解質型燃料電池、最も好ましい態様として、(16)各マニホールドにバネ部材を介して押さえ板を配設させた前記(15)項記載の平板型固体電解質型燃料電池、が挙げられる。このバネ部材としては、窒化ケイ素のような、電池の作動温度でもバネ機能に劣化を生じないものを、コイルバネ、板バネ、皿バネなどの適当な形態で用いるのが好ましい。この押さえ板は、介在させたバネ部材により適切な加圧が付勢されるような間隔で対向配置され、その配置箇所で固定されてもよいし、またそのような配置状態となるようにボルト・ナットで締め付けたり、あるいは押さえ板の外側から外力で加圧してもよい。この外力による加圧は例えば油圧、空気圧などで行われる。

【0018】本発明において好適な固体電解質型燃料電池について以下説明する。先ず各部材については、固体電解質板は酸素イオン伝導性を有するものであれば特に制限されず、例えばイットリア安定化ジルコニア(YSZ)、カルシア安定化ジルコニア(CSZ)のような安定化ジルコニアや部分安定化ジルコニアなどの公知の固体電解質が挙げられる。

【0019】カソードは、酸素や空気などの酸化剤ガス通路側なので、高温下で酸化剤ガスに対して耐食性のある導電性材料、例えば、 $L_{a_x}S_{r_{1-x}}M_{n_0}$ などの導電性複合酸化物粉末を固体電解質板片面に塗布し、ガス透過性となるように多孔質状に形成される。この塗布方法としては、はけ塗り法やスクリーン印刷法などが用いられる。その他、多孔質状膜のカソードの固体電解質板への作成方法としては、CVD法、プラズマCVD法、スパッタ法、溶射法なども使用可能である。

【0020】アノードは、水素などの燃料ガス通路側なので、高温下で燃料ガスに対して耐食性のある導電性材料、例えばNi/ZrO<sub>2</sub>サーメットなどを用い固体電解質板片面にカソードと同様の多孔質状膜形成法を適用して作成される。

【0021】このように両面に各電極すなわちアノード及びカソードを形成した固体電解質板を複数用意し、これらをセパレータを介して集積し、両端の該固体電解質板にそれぞれ端子板を配設することにより、多数のセル10からなる多段直列型の電池が作成される。図4のように、セパレータ44は隣接するセルの電極間を電気的に接続するとともに、両面に溝が設けられ隣接するセルのアノード側及びカソード側のそれぞれのガス通路すなわち燃料ガス通路44a及び酸化剤ガス通路44bが形成されている。各溝は燃料ガス及び酸化剤ガスを供給しうるものであれば特に制限されず、形状や配置等も適宜選定しうるが、通常は図4に示すように、セパレータの上面、下面に設けられる各ガス通路44a、44bは互いに直角方向に配置される。このように配置すれば、セル20を集積後、燃料ガスの入口及び出口、酸化剤ガスの入口及び出口をそれぞれ同じ面上に配置することができ、集積セルとしてガス供給・排出系の構成を簡単かつ容易とすることができる。

【0022】図4のように、電極を設けた固体電解質板41、セパレータ44、各端子板45、46を集積して組み立てるときには、固体電解質板41とセパレータ44又は各端子板45、46との間でガスの漏れ(リーク)がないように封止する必要がある。

【0023】本発明の封止材料は、このような固体電解30質板とセパレータ及び端子板間の封止のために好適に用いられ、その好適使用形態としては、セパレータ及び端子板において、各ガス通路に沿いその面上の両端縁部に封止用溝を設け、これとサイズをマッチさせて封止材料を成形した封止体をこの溝にはめ込んで固定した形態が挙げられる。また、本発明の封止材料が、後述するように、電池本体とマニホールド間の封止に用いられる場合には、前記の封止は、例えばジルコニア系の無機接着剤で接着し、軟化点が約800℃のガラス板やガラスペーストで封止することによってもよい。このガラス板やガラスペーストは電池の作動温度(900~1000℃程度)で適度に軟化しガスを封止する。

【0024】こうして組み立てた電池に燃料ガス及び酸化剤ガスを供給するためには、電池の各ガス通路44a、44bの両端がそれ同一面にくるように配置されているので、それらの面にマニホールドを取り付けばよい。例えば図4に示すように、上記のように組み立てた集積型電池本体を円筒状マニホールド(M)の筒内に挿入し、溝44a、44bの出口が筒内壁に面するように配置し、電池本体とマニホールドの近接箇所(4ヶ所)を封止することにより、各ガス通路44a、44b

のそれぞれの両端がそれぞれマニホールドの円筒壁と電池本体で形成された4つのガス通路すなわち供給燃料ガス通路、排出燃料ガス通路、供給酸化剤ガス通路、排出酸化剤ガス通路と対応することとなる。本発明の封止材料は、また、このような電池本体とマニホールド間の封止のために好適に用いられる。

【0025】本発明の固体電解質型燃料電池として特に好ましいのは、前記電池本体の4つの側面に対向する4つのマニホールドすなわち4分割型マニホールドを配設させたものである。4分割型マニホールドとしては、箱型マニホールドが好ましい。電池本体と箱型マニホールド間には通常ガスケットを介在させる。

【0026】この箱型マニホールド及びガスケットを配設した固体電解質型燃料電池の1例の正面断面概略図を図2に示す。図2において、ベース板29上に、その中央部に電池本体21、その両側に箱型マニホールド22が、共に電池の作動温度で軟化するガラスシート24を介して設けられるとともに電池本体21と箱型マニホールド22間にはガスケット23を介在させ、さらに箱型マニホールド22の奥部の外周に適切な間隔で押さえ治具26が固定して設けられ、箱型マニホールド22と押さえ治具26間には窒化ケイ素バネ25を介在させている。こうして、箱型マニホールドはバネの弾圧によりガスケットひいては電池本体に付勢され押し付けられることになる。各マニホールドには、ベース板29を貫通して燃料ガス供給配管27、燃料ガス排出配管28が接続されている。以上の左右に配設されたマニホールド等の各部材と同様に、前後にもマニホールド等の各部材が配設され、この各マニホールドにも、ベース板29を貫通して酸化剤ガス供給配管、酸化剤ガス排出配管が接続されている。

#### 【0027】

【発明の効果】本発明の固体電解質型燃料電池用封止材料は、高温でも安定で、導電率が小さく絶縁性であり、しかも電池の構成材料間の熱膨張特性の差異に基づく応力あるいは応力歪みを弾性的に吸収あるいは緩和でき、熱サイクルに十分に耐えうる上に、荷重あるいは圧力の変動、高い差圧に十分に耐えることができ、ガスリークを防止でき、高い燃料利用率下で電池出力を向上しうるという顕著な効果を奏する。

#### 【0028】

【実施例】以下、本発明を実施例により詳細に説明する。

#### 実施例1

図1の集積セルの集合様式に従い、10段直列セルの固体電解質型燃料電池を製作した。固体電解質板11にはイットリアを3モル%添加したジルコニアである部分安定化ジルコニアからなる100×100×0.2mmの板状物を用いた。そして、酸素通路側にLa<sub>0.9</sub> Sr<sub>0.1</sub>MnO<sub>3</sub>粉末(平均粒径約5μm)をはけ塗り法

で厚さ0.1mmに塗布してカソード13とし、水素通路側にNi/ZrO<sub>2</sub>(10/1重量比)のサーメット混合粉末をはけ塗り法で厚さ0.1mmに塗布してアノード12とした。セパレータ14及び端子板15,16にはインコネル600を用いた。セパレータ及び端子板の寸法は100×100mmで高さ2.4mm、溝の深さ0.5mmとした。

【0029】この固体電解質板11とセパレータ14を交互に積層し、両端の該固体電解質板にそれぞれ端子板を配設し、固体電解質板11とセパレータ14及び端子板15,16の間に軟化点が約800℃のガラス板を挟んでガス封止用とした。このガラス板には電池の作動温度(1000℃)で水素に対して耐還元性があり、空気に対して耐酸化性があり、また耐水蒸気性のあるものを選ぶ。このガラス板は電池の作動温度で軟化してガスを封止する。

【0030】こうして集積した電池にマニホールドを図2のように設置し、マニホールドと電池の間には、厚さ1mmの、SiO<sub>2</sub>40重量%及びAl<sub>2</sub>O<sub>3</sub>60重量%の組成を有し、かつ多孔度が90%で電気伝導度が10<sup>-5</sup>Ω<sup>-1</sup>cm<sup>-1</sup>のセラミックス多孔体を挟み込み、ガスケットとともに、マニホールドを電池本体に弾圧的にガスケット面への加圧1.0kgf/cm<sup>2</sup>で押し付けるようにした。この押し付けは、マニホールドとその外側に固定設置した押さえ治具の間に窒化ケイ素バネのような付勢バネを介在させることにより行った。電気の取り出し部には白金リード線を溶接し、電気的に接続した。

【0031】このようにして作製した固体電解質型燃料電池を加熱した。室温から150℃までは1℃/minで昇温し、塗布電極の溶媒を蒸発させた。150~350℃までは1.5℃/minで昇温した。350℃以上では水素通路側には、アノードの酸化を防止するため、窒素ガスを流し、1℃/minで1000℃まで昇温した。

【0032】1000℃に達した後に、ガス出口流量を膜流量計で測定したところ、アノード側、カソード側とも外部リーク量は1~2%程度であった。その後、1000℃に保持してアノード側に水素、カソード側に酸素を流し、発電を開始した。開放電圧は12.5Vで、ガスクロスリークは水素で0.1%以下であった。この電池の放電特性を表1に示す。

#### 【0033】

#### 【表1】

電圧(V)	電流(A)
12.5	0.0
11.0	0.8
10.0	2.1
9.0	6.3
8.0	11.3
7.0	16.0

【0034】次に、この電池の最大燃料利用率を測定したところ、8.2%となった。

【0035】実施例2

図3の集合様式に従い、10段直列セルの固体電解質型燃料電池を製作した。固体電解質板31にはイットリアを3モル%添加したジルコニアである部分安定化ジルコニアからなる $100 \times 100 \times 0.2$ mmの板状物を用いた。そして、酸素通路側に $\text{La}_{0.9}\text{Sr}_{0.1}\text{MnO}_3$ 粉末（平均粒径約 $5\mu\text{m}$ ）をはけ塗り法で厚さ0.1mmに塗布してカソード33とし、水素通路側に $\text{Ni/ZrO}_2$ （10/1重量比）のサーメット混合粉末をはけ塗り法で厚さ0.1mmに塗布してアノード32とした。セパレータ34及び端子板35, 36にはインコネル600を用いた。セパレータ及び端子板の寸法は $100 \times 100$ mmで高さ2.4mm、溝の深さ0.5mmとした。また、セパレータ34の両面及び端子板35, 36の片面の両端には所定ガス通路に沿って封止用溝37を設け、その深さを0.8mmとした。

【0036】この固体電解質板31とセパレータ34を交互に集積し、両端の該固体電解質板にそれぞれ端子板35, 36を配設し、固体電解質板31とセパレータ34及び端子板35, 36の間には、厚さ1mmの、 $\text{SiO}_2$ 40重量%及び $\text{Al}_2\text{O}_3$ 60重量%の組成を有し、かつ多孔度が90%で電気伝導度が $10^{-5}\Omega^{-1}\text{cm}^{-1}$ のセラミックス多孔体38を封止用溝37に埋め込み、ガスケットとした。

【0037】こうして集積した電池にマニホールドを図2のように設置し、マニホールドと電池の間に軟化点が約800℃のガラス板を挟んでガス封止用とした。このガラス板には電池の作動温度（1000℃）で水素に対して耐還元性があり、空気に対して耐酸化性があり、また耐水蒸気性のあるものを選ぶ。このガラス板は電池の作動温度で軟化してガスを封止する。電気の取り出し部には白金リード線を溶接し、電気的に接続した。

【0038】このようにして作製した固体電解質型燃料電池を加熱した。室温から150℃までは $1\text{^\circ C/min}$ で昇温し、塗布電極の溶媒を蒸発させた。150~350℃までは $1.5\text{^\circ C/min}$ で昇温した。350℃以上では水素通路側には、アノードの酸化を防止するため、窒素ガスを流し、 $1\text{^\circ C/min}$ で1000℃まで昇温した。

【0039】1000℃に達した後に、ガス出口流量を膜流量計で測定したところ、アノード側、カソード側とも外部リーク量は5~7%程度であった。その後、1000℃に保持してアノード側に水素、カソード側に酸素を流し、発電を開始した。開放電圧は12Vで、ガスクロスリーク量は水素で0.02%以下であった。この電池の放電特性を表2に示す。

【0040】

【表2】

電圧 (V)	電流 (A)
12.0	0.0
11.0	0.5
10.0	1.2
9.0	3.0
8.0	9.1
7.0	13.3

【0041】次に、この電池の最大燃料利用率を測定したところ、7.0%となった。

【0042】実施例3

10 図3の集合様式に従い、10段直列セルの固体電解質型燃料電池を製作した。固体電解質板31にはイットリアを3モル%添加したジルコニアである部分安定化ジルコニアからなる $100 \times 100 \times 0.2$ mmの板状物を用いた。そして、酸素通路側に $\text{La}_{0.9}\text{Sr}_{0.1}\text{MnO}_3$ 粉末（平均粒径約 $5\mu\text{m}$ ）をはけ塗り法で厚さ0.1mmに塗布してカソード33とし、水素通路側に $\text{Ni/ZrO}_2$ （10/1重量比）のサーメット混合粉末をはけ塗り法で厚さ0.1mmに塗布してアノード32とした。セパレータ34及び端子板35, 36にはインコネル600を用いた。セパレータ及び端子板の寸法は $100 \times 100$ mmで高さ2.4mm、溝の深さ0.5mmとした。また、セパレータ34の両面及び端子板35, 36の片面の両端には所定ガス通路に沿って封止用溝37を設け、その深さを0.8mmとした。

20 【0043】この固体電解質板31とセパレータ34を交互に集積し、両端の該固体電解質板にそれぞれ端子板35, 36を配設し、固体電解質板31とセパレータ34及び端子板35, 36の間には、厚さ1mmの、 $\text{SiO}_2$ 40重量%及び $\text{Al}_2\text{O}_3$ 60重量%の組成を有し、かつ多孔度が90%で電気伝導度が $10^{-5}\Omega^{-1}\text{cm}^{-1}$ のセラミックス多孔体38を封止用溝37に埋め込み、ガスケットとした。

30 【0044】こうして集積した電池にマニホールドを図2のように設置し、マニホールドと電池の間に厚さ1mmの、 $\text{SiO}_2$ 40重量%及び $\text{Al}_2\text{O}_3$ 60重量%の組成を有し、かつ多孔度が90%で電気伝導度が $10^{-5}\Omega^{-1}\text{cm}^{-1}$ のセラミックス多孔体を埋め込み、ガスケットとするとともに、マニホールドを電池本体に弾圧的にガスケット面への加圧 $1.0\text{kgf/cm}^2$ で40 押し付けるようにした。この押し付けは、マニホールドとその外側に固定設置した押さえ治具の間に窒化ケイ素バネのような付勢バネを介在させることにより行った。電気の取り出し部には白金リード線を溶接し、電気的に接続した。

40 【0045】このようにして作製した固体電解質型燃料電池を加熱した。室温から150℃までは $1\text{^\circ C/min}$ で昇温し、塗布電極の溶媒を蒸発させた。150~350℃までは $1.5\text{^\circ C/min}$ で昇温した。350℃以上では水素通路側には、アノードの酸化を防止するため、窒素ガスを流し、 $1\text{^\circ C/min}$ で1000℃まで昇温し

た。

【0046】1000℃に達した後に、ガス出口流量を膜流量計で測定したところ、アノード側、カソード側とも外部リーク量は1~2%程度であった。その後、1000℃に保持してアノード側に水素、カソード側に酸素を流し、発電を開始した。開放電圧は12.7Vで、ガスクロスリーク量は水素で0.02%以下であった。この電池の放電特性を表3に示す。

【0047】

【表3】

電圧 (V)	電流 (A)
12.7	0.0
11.0	1.2
10.0	3.0
9.0	7.2
8.0	14.4
7.0	22.0

【0048】次に、この電池の最大燃料利用率を測定したところ、87%となった。

【0049】比較例

図4に示すような従来の方法で電池を設置し、封止材としてガラス（多孔度0.1%未満）を用いた10段直列セルでは、実施例1と同様の測定で外部リーク量は1%程度、開放電圧は11.5V、ガスクロスリーク量は水素で3%程度であった。このセルの放電特性を表4に示す。

【0050】

【表4】

電圧 (V)	電流 (A)
11.5	0.0
10.0	0.8
9.0	1.5
8.0	7.2
7.0	10.8

(7) 12

【0051】次に、このセルの最大燃料利用率を測定したところ、60%と低かった。

【図面の簡単な説明】

【図1】平板型固体電解質型燃料電池の1例の集合様式を示す分解説明図。

【図2】本発明の好適な平板型固体電解質型燃料電池の1例の正面断面概略図。

【図3】本発明の平板型固体電解質型燃料電池の1例の集合様式を示す分解説明図。

10 【図4】円筒状型マニホールドを備えた平板型固体電解質型燃料電池の1例の斜視説明図。

【符号の説明】

11, 31, 41 固体電解質板

12, 32, 42 アノード

13, 33, 43 カソード

14, 34, 44 セパレータ

14a, 44a 燃料ガス通路

14b, 44b 酸化剤ガス通路

15, 16, 35, 36, 45, 46 端子板

20 21 電池本体

22 箱型マニホールド

23 ガスケット

24 ガラスシート

25 窒化ケイ素バネ

26 押さえ治具

27 燃料ガス供給配管

28 燃料ガス排出配管

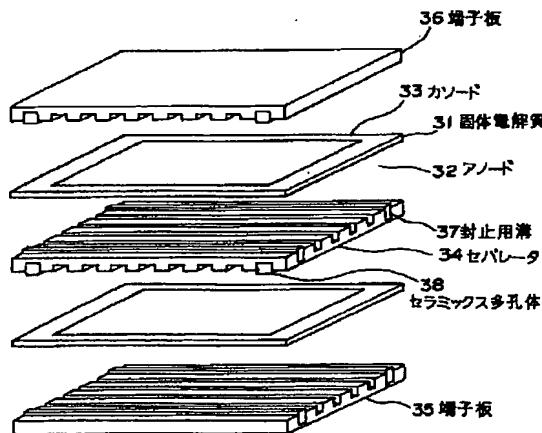
29 ベース板

37 封止用溝

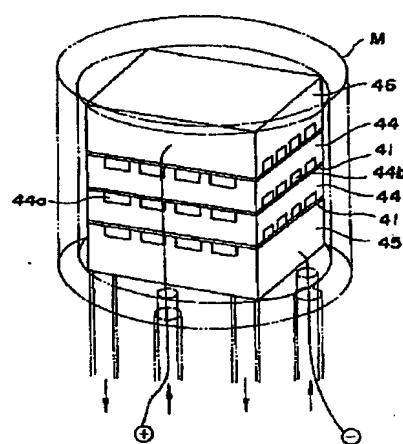
30 38 セラミックス多孔体

M 円筒状マニホールド

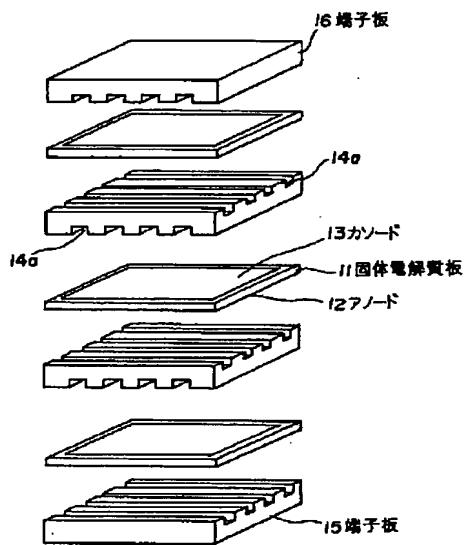
【図3】



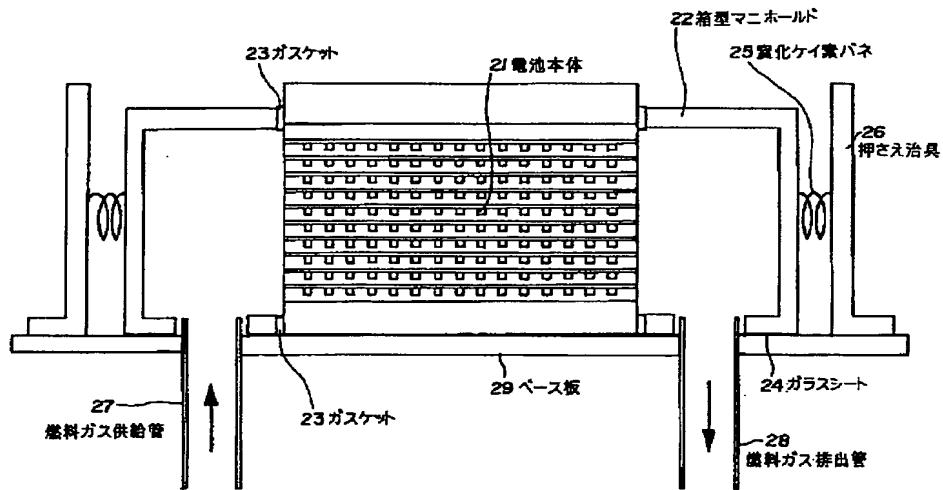
【図4】



【図1】



【図2】



フロントページの続き

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